DIELECTRIC PROPERTIES OF COMPRESSED RUBIDIUM BI SULPHATE POWDERS

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ABSTRACT

The dielectric constant of powders of $RbHSO_4$ of different particle size has been studied at 1 MHz over a wide range of temperatures. It is observed that the dielectric constant decreases with decreasing particle size. Even for the biggest particle size, the measured dielectric constant is less than the theoretically expected value for polycrystalline sample. Useful information about the existence of surface layer, its dielectric constant and thickness has been established. In the present sample of $RbHSO_4$, the surface layer thickness and its dielectric constant are found to be 45 μm, and 20 respectively.

1. INTRODUCTION

The studies on erroelectric transition, vibration sepectra and the crystal structure of $RbHSO_4$ have been reported in literature[1-3]. But no information is available on the dielectric behaviour of a powder of $RbHSO_4$ for various particle sizes. In the case of $BaTiO_3$[4], $AgNa(NO_2)_2$[5] and $(NH_4)_2SO_4$[6], the dielectric constant is found to decrease with decreasing particle size. The surface layer effects in $(NH_4)_2SO_4$ and $AgNa(NO_2)_2$ were studied by Abhaimansingh and Bawa[6], and S. S. Bawa and L. K. Khanna[5] respectively.

In the present communication, the dielectric measurements on $RbHSO_4$ powder of varying particle sizes ranging from 104 μm to 500 μm from liquid nitrogen temperature to 62° C at 1 MHz are reported. The experimental values of the dielectric constant are compared with the values for polycrystalline sample. The surface layer thickness and its dielectric constant are deduced.

2. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

The sample is prepared in the laboratory as suggested by Pepinsky and Vedam[1]. The experimental setup consists of Franklin oscillator in combination with variable GR precision condensers of values 110–1100 PF and 11–110 PF. The change of capacitance

has been measured to an accuracy of ± 0·002 PF. The static dielectric constants were determined at 1 MHz by the above technique.

3. RESULTS AND DISCUSSION

All calculations are carried out on computer IBM 1130. Variation of experimental values of dielectric constant with temperature for different particle sizes of $RbHSO_4$ is shown in Fig. 1. Between liquid nitrogen
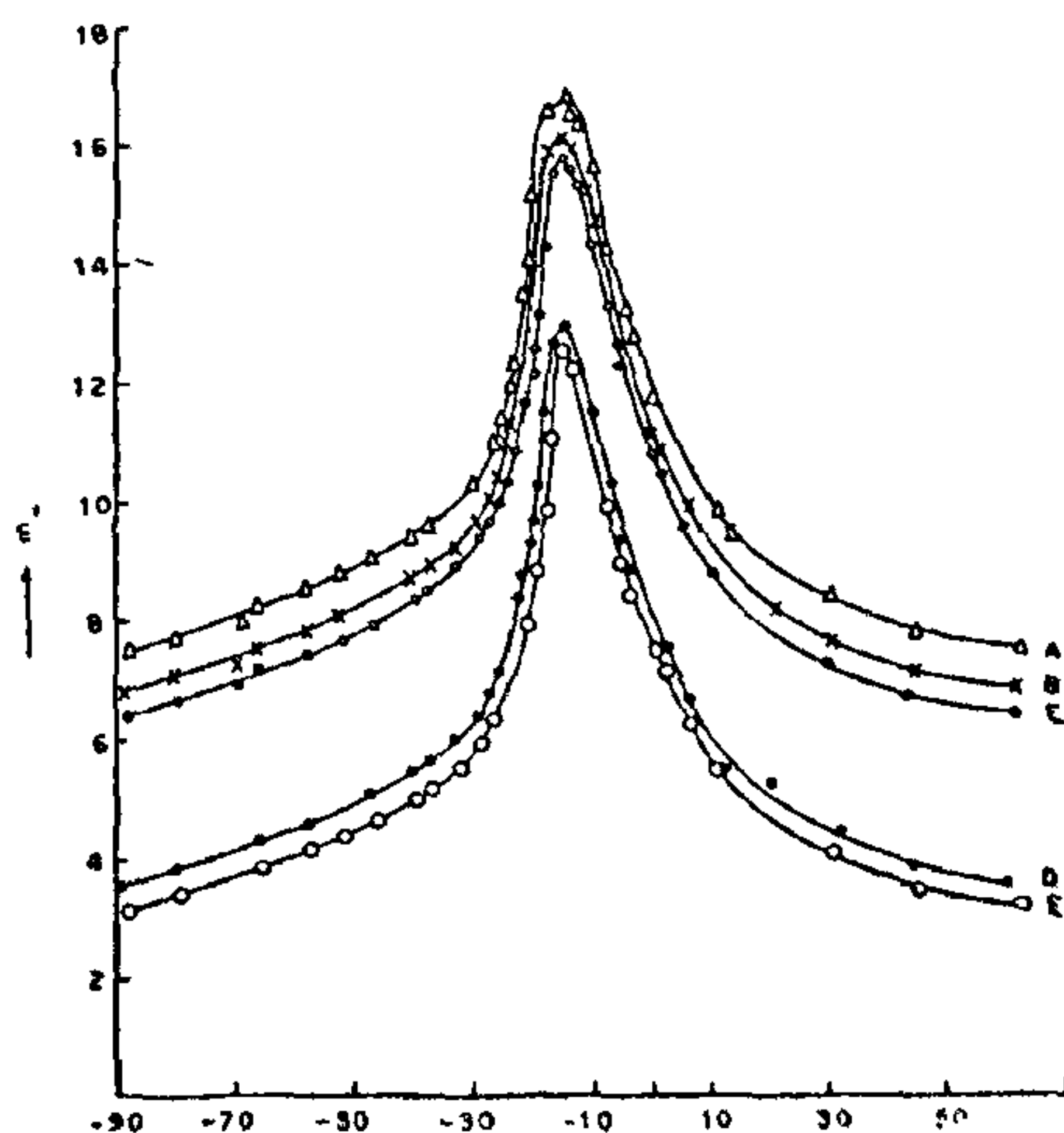

FIG. 1. Dielectric constant as a function of temperature for five compressed powders of Rb HSO₄. A, 350–500 μm; B, 250–350 μm; C, 177–250 μm; D, 125–177 μm; E, 104–125 μm.

temperature to $-90°$ C the variation of dielectric constant with temperature is found to be similar to that of the single crystal. Hence, this temperature range is not shown in Fig. 1. It is observed that, the dielectric constant decreases with decreasing particle size. The dielectric anomaly has been observed at $-15°$ C for different particle sizes as in the case if single crystal. However, the curve is not sharp as that of the single crystal.

The experimental values of the dielectric constant were corrected for porosity by using the following formulae[7,8].

$$\epsilon_s = \{1/\delta\,(\epsilon_p^{1/3} - 1) + 1\}^3\,(L - L - L)^7 \tag{3.1}$$

and

$$\epsilon_s = \frac{3\epsilon_s\delta + 2\epsilon_p\,(\epsilon_p - 1)}{3\epsilon_p\,\delta - (\epsilon_p - 1)}\;(Bottcher)^8 \tag{3.2}$$

where ϵ_s is the corrected value for non-porous sample, ϵ_p the erperimental value for porous sample and δ the packing fractios. The following modified Bruggman[9] equation is used to compare the experimental value of ϵ_p with the theoretically expected value ϵ^* for poly-crystalline sample.

$$\frac{\epsilon^* - 1}{\epsilon^*} = \frac{\epsilon_1 - 1}{2\epsilon^* + \epsilon_1} + \frac{\epsilon_2 - 1}{2\epsilon^* + \epsilon_2} + \frac{\epsilon_3 - 1}{2\epsilon^* + \epsilon_3} \tag{3.3}$$

where ϵ^* is the dielectric constast for the polycrystalline sample, ϵ_1, ϵ_2 and ϵ_3 are the values of the dielectric constant along the three axes of single crystal[1].

Temperature variation of experimental value of dielectric constant (ϵ_p), the porosity corrected value (ϵ_s) and the theoretical value (ϵ^*) have been shown is Fig. 2 for the sample of particle size range (350-500 μm). This figure indicates that the theoretically predicted values are greater than those obtained experimentally and also by porosity corrected values. It is found that the dielectric constant of compressed powders of ferroelectric material is lower than the theoretically expected values indicating a particle size depen-

dence. This can be explained by assuming that a defective surface layer is formed due to the mechanical discontinuity in the periodic lattice[4]. Such a surface layer has lower values of dielectric constant and spontaneous polarization than the bulk[10].
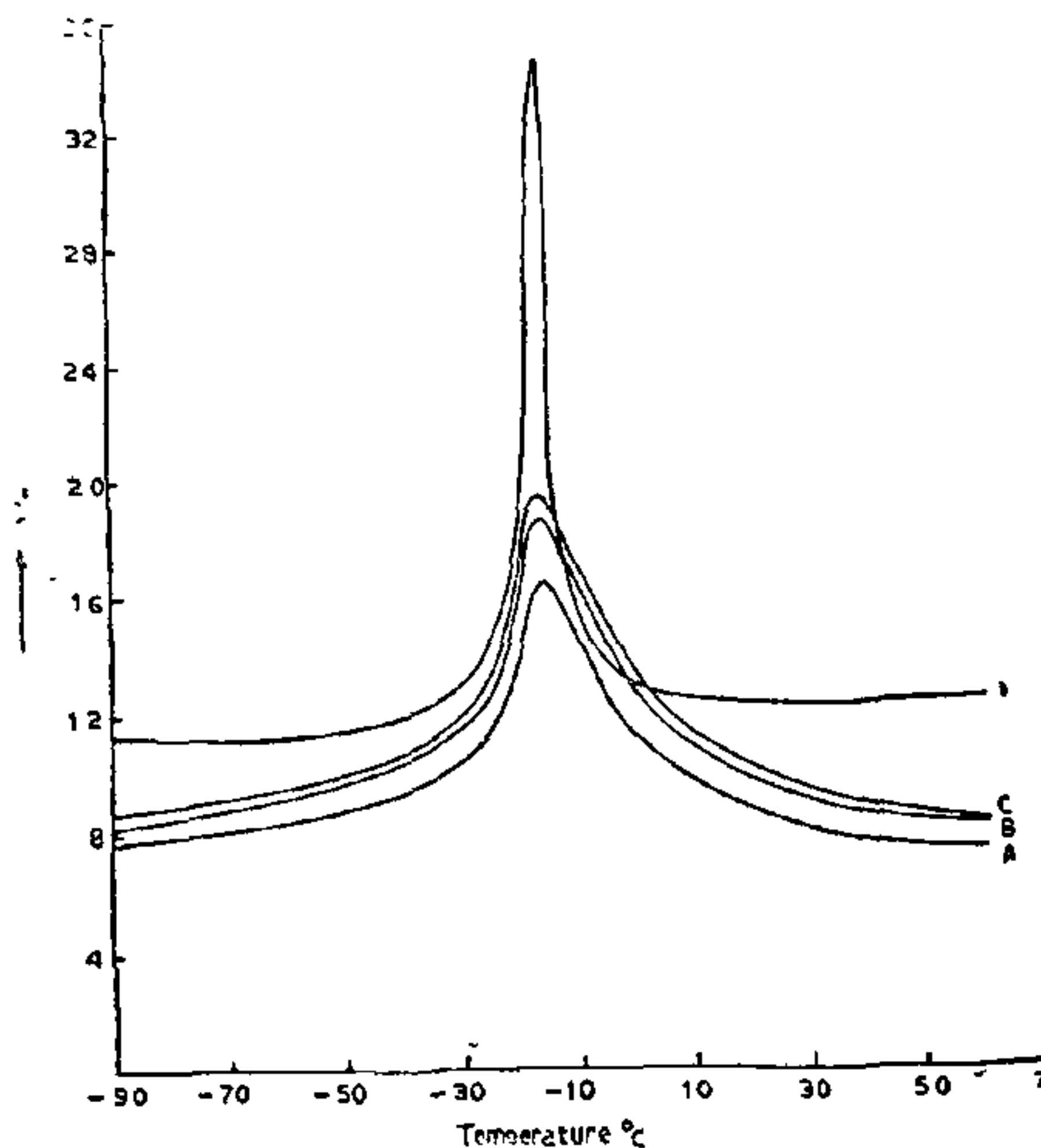

FIG. 2. Dielectric constant as a function of temperature for a polycrystalline sample. A, Experimental curve for a sample of 350-500 μm particle size ($\delta = 0.9184$); B and C, corrected experimental curves porosity using Bottcher and Looyenga formulae respectively; D, Theoretically predicted curve.

Thickness of the surface layer and its dielectric constant have been calculated from the porosity corrected values and the dielectric constant of the non-defective polycrystalline sample. By assuming the particle to be of spherical shape and using the Bottchers[8] relation, the surface layer thickness and its dielectric constant can be expressed as

$$\epsilon_L = \frac{\epsilon_s\{\epsilon^*\,(3\delta - 1) - 2\,\epsilon_s\}}{\{\epsilon_s\,(3\delta - 2) - \epsilon^*\}} \tag{3.4}$$

$$\delta = \left\{\frac{(a - 2d)}{a}\right\}^3 \tag{3.5}$$

where ϵ_s is the dielectric constant of normal density of the solid, ϵ_L the surface layer dielectric constant, ϵ^* the dielectric constant

of the non-defective bulk, 'a' the size of the crystalline and 'd' the surface layer thickness.

The following procedure is adopted for calculating the surface layer thickness and its dielectric constant. Two samples of particle size (ranges 104–125 μm and 125–177 μm) have been selected with an average particle size of 114 μm and 151 μm respectively. The measured dielectric constant for these ranges are corrected for the porosity and taken as the dielectric constant of non-porous samples. The surface layer thickness was then varied in steps of 0·1 μm. From the known values of ϵ^{*} and ϵ, the surface layer thickness and its dielectric constant have been calculated using equations (3.4) and (3.5). In the present sample the surface layer thickness which yields equal values of surface layer dielectric constant of 20 was found to be 45 μm. Similar calculation carried out for other temperatures showed little temperature dependence of surface layer parameters.

Further verification of the surface layer parameters was made by calculating the lower and upper bounds of the three phase heterogeneous mixture[11].

$$\epsilon_1^{*} = \epsilon_1 + A_2/(1 - \alpha_1 A_1) \qquad (3\ 6)$$

$$\epsilon_3^{*} = \epsilon_3 + A_3/(1 - \alpha_3 A_3) \qquad (3.7)$$

where

$$\alpha_1 = 1/3\epsilon_1 \ : \ \alpha_3 = 1/3\epsilon_3$$

$$A_1 = \sum_{t=2,3} v_t / \left\{ (\epsilon_t - \epsilon_1)^{-1} + \alpha_1 \right\}$$

$$A_3 = \sum_{t=1,2} v_t / \left\{ (\epsilon_t - \epsilon_1)^{-1} + \alpha_3 \right\}$$

where ϵ_1^{*} and ϵ_3^{*} are the lowest upper bound and highest lower bound respectively, v_t the fractional volume occupied by the 't' phase such that $\sum_{t=1,2,3} v_t = 1$. The calculated bounds are shown in Fig. 3, for a sample of particle size 114 μm (range 104–125 μm) along with the experimestal curve. It is evident from the figure that the experimental values lie within the calculated bounds. It may be concluded that the calculated values of surface layer thickness and its dielectric constant are of the right order.
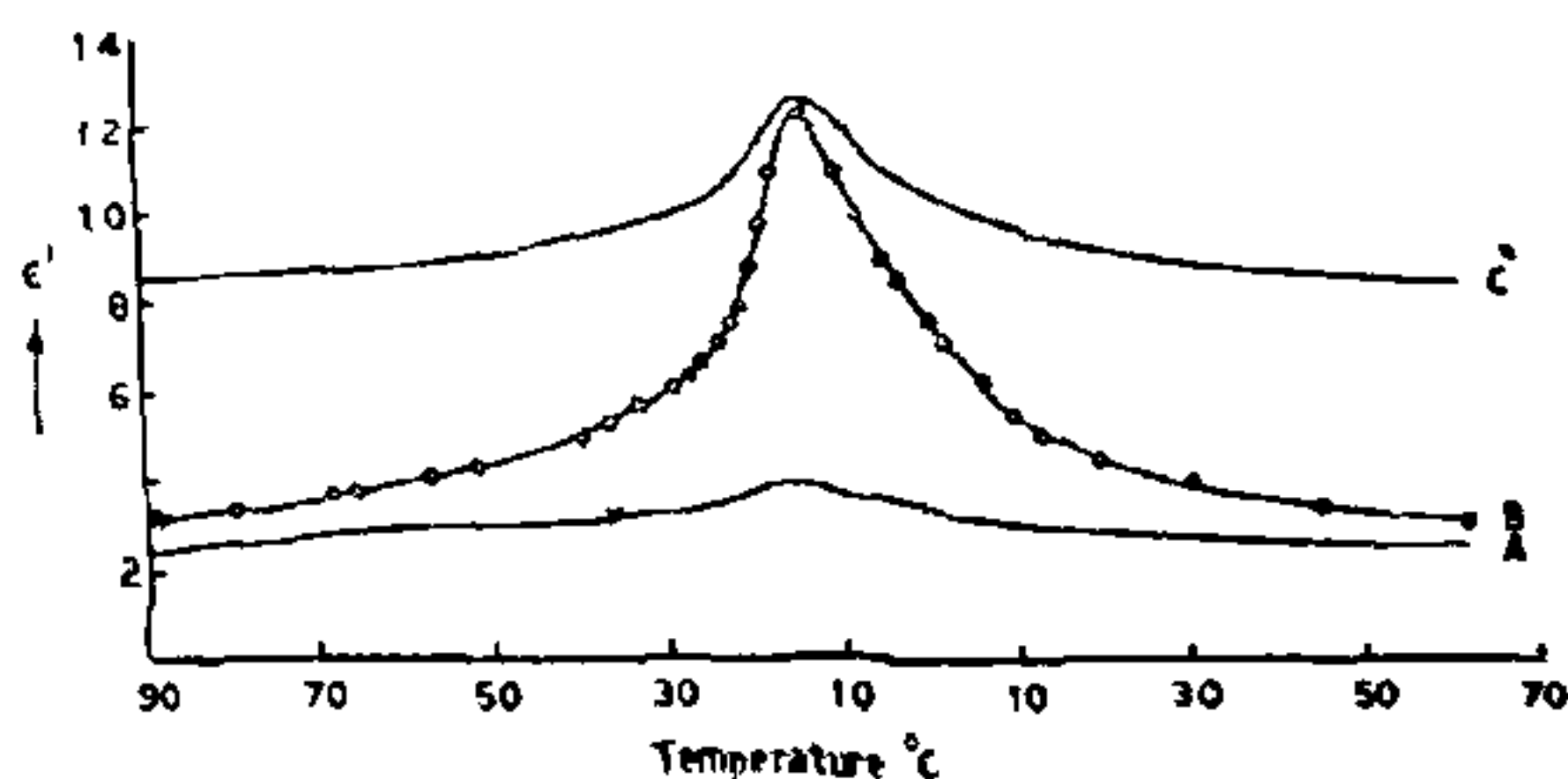

FIG. 3. Expected bounds for dielectric constant of three phase hetrogeneous mixture. Curve B is the experimental curve (particle size 104–125 μm packing fraction 0·8274). Curves A and C are the lower and upper bounds respectively.

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